

SIMULTANEOUS HYDROCARBON REFORMING, CARBON DIOXIDE SEQUESTRATION AND HYDROGEN SEPARATION USING DENSE INORGANIC MEMBRANES

Topic: Separation and Capture
Subtopic: Membranes

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INTRODUCTION

Oxygen transport membranes, under development at Eltron Research Inc., facilitate the selective transport of oxygen from the atmosphere to desired oxidation reaction sites. The membranes can be incorporated into Catalytic Membrane Reactors (CMRs) where, for example, exothermic hydrocarbon partial oxidation chemistries can proceed. The oxygen transport membranes eliminate the need for oxygen separation plants.

This membrane technology can be used for the spontaneous reforming of natural gas, petroleum, biomass, and coal into synthesis gas, a mixture of hydrogen and carbon monoxide. Application of water-gas shift chemistry leads to conversion of carbon monoxide and steam to carbon dioxide and hydrogen.

Hydrogen transport membranes designed for the efficient separation of hydrogen from the hydrogen containing feedstreams discussed above are also being developed within our company. These dense hydrogen transport membranes possess hydrogen permeabilities one order of magnitude higher than palladium. Furthermore, these membranes are far less expensive. Self-supporting wafers of these hydrogen transport membranes have been successfully operated for thousands of hours at ambient pressure and for hundreds of hours under differential pressure of up to 31 bar (450 psi) without failure. Hydrogen fluxes across the membranes of up to $360 \text{ mL min}^{-1} \text{ cm}^{-2}$ (STP) have been realized.

OXYGEN TRANSPORT MEMBRANES FOR HYDROCARBON REFORMING

Dense mixed oxygen anion and electron conducting ceramic membranes are derived from oxygen-deficient metal oxides possessing the general formula $A_{2-x}A'_xB_{2-y}B'_yO_{5+z}$. This CMR technology facilitates spontaneous reforming of natural gas (methane), liquid hydrocarbon fuels and coal into synthesis gas feeds, as shown schematically in Figure 1.

To achieve high oxygen flux in membrane materials which possess high stability, Eltron¹⁻⁹ has developed mixed oxygen anion and electron conducting membranes $A_{2-x}A'_xB_{2-y}B'_yO_{5+z}$ where: A is an alkaline earth metal ion or mixture of alkaline earth metal ions; A' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the lanthanide series or is yttrium; B is a metal ion or mixture of metal ions wherein the metal is selected from the group consisting of 3d transition metals and the Group 13 metals; B' is a metal ion or mixture of metal ions where the metal is selected from the group consisting of the 3d transition metals, the lanthanides and yttrium.

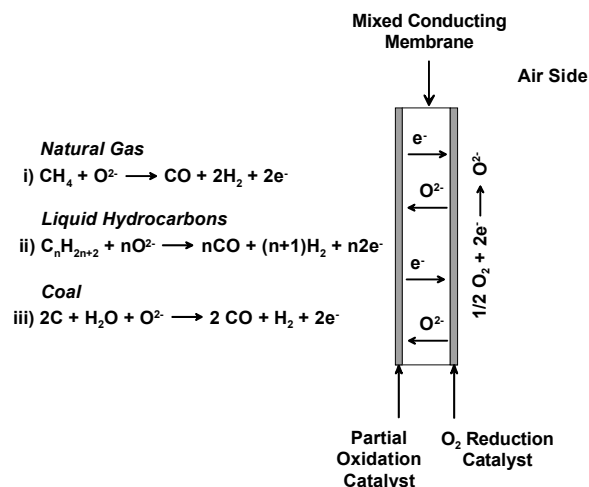
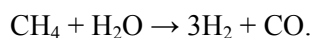


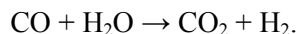
Figure 1. Schematic of spontaneous processes occurring on the membrane partial oxidation and reduction surfaces for the reforming of i) natural gas, ii) liquid hydrocarbons, and iii) coal into synthesis gas.

The rationale for selecting specific A and B lattice substituents has evolved from work performed at Eltron¹⁰⁻¹⁴ which identified clear correlations between crystallographic and thermodynamic parameters relating to the activation energy for ionic transport. These parameters include: 1) the average metal-oxygen bond energy within the lattice, 2) lattice free volumes, obtained by subtracting the ionic volumes of cations and O^{2-} in the unit cell from the overall crystallographic unit cell, 3) the parameter $r_{critical}$ (r_c) which corresponds to the radius of the opening between the two A site cations and one B site cation through which the mobile anion must pass, and 4) lattice polarizability towards ionic migration.

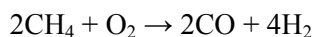
Of all the potential applications for mixed oxygen anion and electronic conducting materials, the partial oxidation of methane to syngas is one of the most commercially important. Syngas can serve as a precursor for a variety of products such as methanol, higher alcohols or Fischer-Tropsch products. Current commercially available technology for syngas production from natural gas is based on the endothermic steam reforming reaction represented by:



Additional hydrogen can be produced by reacting CO with steam via the water-gas shift reaction:



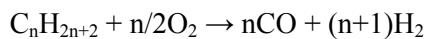
Alternatively, the exothermic methane partial oxidation reaction:



can proceed using the mixed conducting membranes, with oxygen being separated from the atmosphere at the membrane reducing surface for subsequent participation in the natural gas partial oxidation reforming reaction at the membrane oxidizing surface.

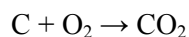
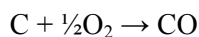
CMRs have been successfully operated under ambient pressure conditions for over one year at 900°C for natural gas reforming. Performance realized for ambient pressure CMRs may be summarized as follows: Syngas Production Rate: 60 mL min⁻¹ cm⁻², Equivalent O₂ Flux: ~ 10-12 mL min⁻¹ cm⁻² (corresponding oxygen anion conductivity > 1S cm⁻¹), H₂:CO Ratio: ~ 1.9 - 2.0, CO Selectivity: >96%, Throughput Conversion: 90% CH₄, 70% O₂ (air). Additionally, Eltron has accumulated over eight years of experimental experience for CMRs operating at elevated temperatures with a 250 psi pressure differential between the hydrocarbon and the air side of the membrane.

The spontaneous reforming of liquid hydrocarbon fuels into H₂/CO mixtures provides a feedstock compatible for subsequent electrochemical oxidation in the anode compartment of a Solid Oxide Fuel Cell (SOFC). The overall reforming process may be represented by:



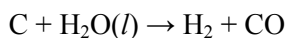
Ceramic membrane partial oxidation process operating conditions have been systematically evaluated using: i) the respective logistic fuel model constituents dodecane, hexadecane, octane, branched chain hydrocarbons and aromatic hydrocarbons, and ii) representative diesel and jet fuels. At 900°C, synthesis gas production rates approaching 40 mL min⁻¹ cm⁻² were achieved when converting dodecane as a simulant for diesel fuel. Throughput conversions were 99%. This corresponded to an oxygen flux rate across the membrane >6.3 mL min⁻¹ cm⁻². CMRs were also operated directly on both diesel and jet fuels. For diesel fuel, the synthesis gas production rate was >27 mL min⁻¹ cm⁻² with stoichiometric (~100%) throughput conversion. In the case of jet fuel, the synthesis gas production rate was >22 mL min⁻¹ cm⁻² with a throughput conversion of >80%. Diesel fuel partial oxidation to synthesis gas at a rate of 27 mL min⁻¹ cm⁻² when used for SOFC fuel would produce an equivalent current of 3.9A/cm². Assuming the SOFC operates at 0.75V per cell, this would correspond to a power output of 2.9W/cm² of membrane reactor surface area.

Eltron's CMR technology is also being applied towards oxygen separation for reaction with coal fines. Membrane-based coal gasifiers are being developed for both the direct gasification of coal with mediated oxygen anions as well as for coal gasification with molecular oxygen evolved from the membrane's oxidation catalyst. This is requiring the development of two oxidation strategies. Gasification reactions occurring between coal and mediated oxygen are a combination of partial oxidation and complete combustion of coal as shown below:



where C is used as an empirical representation for coal. Using coal as the sole component of the feedstream requires resolution of two issues. The first is that since the above reactions are highly exothermic ($\Delta H = -110.5$ J/mol and -393.5 J/mol respectively), any reactor system using this approach must be designed for proper heat transfer. Second, the products of this process are not very versatile. The CO is useful only as a fuel or as a feedstock in chemical processes requiring carbon monoxide.

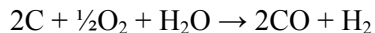
In order to address these two issues, steam is being added to the coal feedstream. Since the production of steam and the steam reforming of coal, symbolized below,



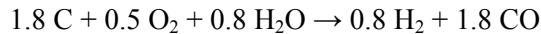
is endothermic ($\Delta H = 175.4$ J/mol), this process can be used to absorb the heat generated by the exothermic coal oxidation process.

Furthermore, the introduction of steam serves to form hydrogen. The resulting product, a mixture of hydrogen and carbon monoxide, has a high Btu value making it more valuable as a fuel or as a feedstock for the production of liquid fuels such as methanol or diesel.

The following reaction, which is a combination of the partial oxidation and steam reforming of coal, summarizes the process being developed at Eltron utilizing CMRs with a humidified coal feed stream to yield a product containing hydrogen and carbon monoxide.



For the process to be self-sustaining it needs to be operated either exothermally or at the thermoneutral point. The thermoneutral point reaction is represented by:



which yields a product gas with a $\text{H}_2:\text{CO}$ ratio of 0.44:1.

For fixed-bed coal gasifiers, coal gasification rates as high as $4.9 \text{ mL min}^{-1} \text{ cm}^{-1}$ (61.3 mL/min) were obtained. A corresponding oxygen depletion of greater than 60% was found on the air side confirming the utility and role of the mixed conducting membrane. There was never any sign of melting of the coal ash which was recovered following experimentation. This indicates that this membrane-based gasifier operates below the slagging temperature. Coal gasification production rates of up to $17.8 \text{ mL min}^{-1} \text{ cm}^{-2}$ (188 mL/min) were achieved with a continuous feed reactor operating at 900°C . Experimentation without an oxidation/reforming catalyst on the surface of the membrane showed similar results to the case when a catalyst layer was deposited on the oxidation surface. This indicates that intimate contact between coal, oxygen anions, and steam on the membrane surface is not essential, greatly simplifying future gasifier designs.

HYDROGEN TRANSPORT MEMBRANES

Eltron is also developing low cost dense hydrogen transport membrane technology towards the goal of integrating with water-gas shift chemistry so as to provide separate streams of hydrogen and carbon dioxide. This provides an opportunity for carbon dioxide sequestration while simultaneously producing an environmentally benign energy feedstock.

Principles behind this approach are shown in Figure 2. These membrane materials possess hydrogen permeabilities one order of magnitude higher than palladium, under equivalent experimental conditions. Furthermore, the membrane constituents are more than two orders of magnitude less expensive than palladium. The performance of one of these membranes operating at 435°C with 30 bar (430 psi) across the membrane is shown in Figure 3.

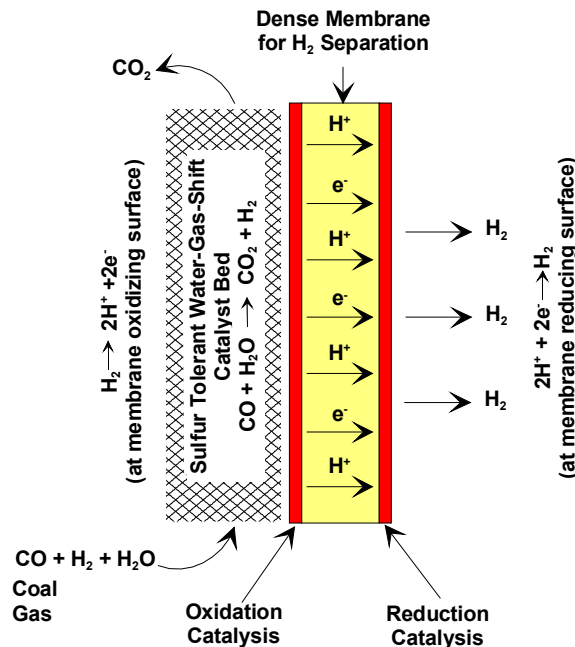


Figure 2. Combined water-gas shift/hydrogen transport membrane for removing hydrogen from CO/H_2 mixtures.

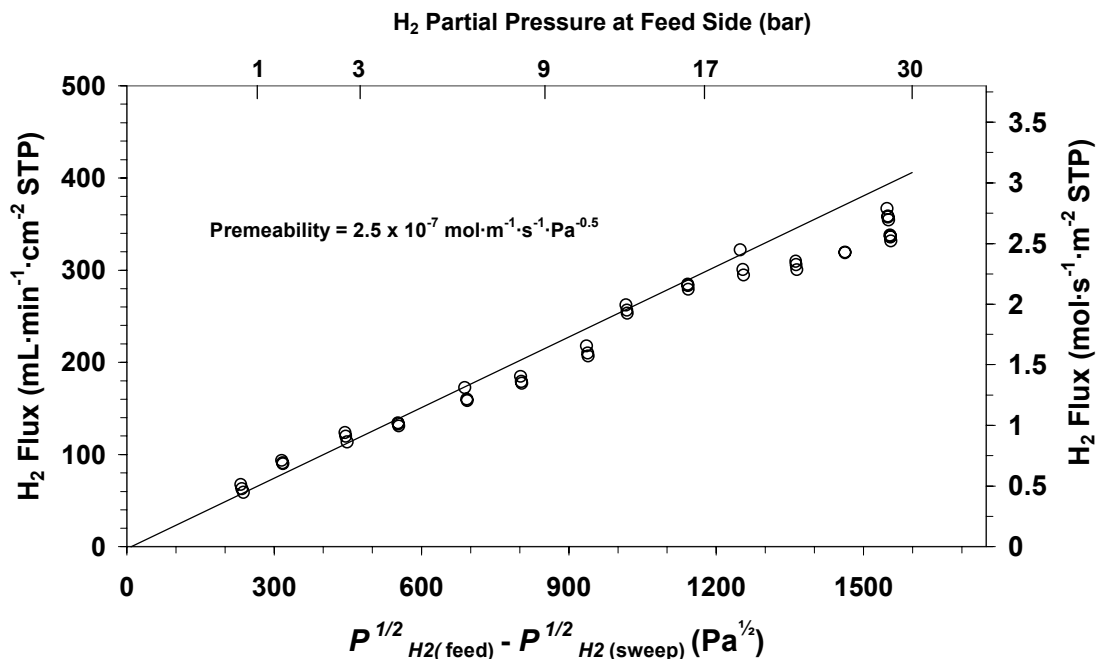


Figure 3. Hydrogen transport membrane at 435°C with H₂ feed varying between 40% H₂ / 60% He and 94% H₂ / 6% He. Maximum H₂ flux 360 mL·min⁻¹·cm⁻² (STP). Maximum differential pressure 430 psi.

ECONOMIC ISSUES

Using conventional technology, hydrocarbon reforming can constitute up to 63% of hydrogen production costs.¹⁵ By substituting conventional endothermic steam reforming by oxygen supplied through our oxygen transport membrane technology, this facilitates an exothermic hydrocarbon reforming process thereby lowering reforming costs by 30%. Using preliminary performance and cost figures for our hydrogen transport membranes, the technology may have the potential to lower hydrogen separation costs by 30% compared to PSA.¹⁵ Using assumptions published in the literature,¹⁶ we can estimate hydrogen costs using combined oxygen and hydrogen transport membranes at \$5/MM Btu or \$0.55/kg.

MEMBRANES AND THE HYDROGEN ECONOMY

We have pursued numerous technical strategies towards achieving efficient hydrogen generation. This has included electrolytic, photoelectrochemical, and membrane based approaches.¹⁷⁻¹⁹ Because of the intrinsic efficiency limitations associated with both electrolytic and photoelectrochemical processes, we conclude that in the foreseeable future, hydrogen for the hydrogen economy will need to rely upon carbonaceous feedstocks, such as natural gas, petroleum, biomass and coal. Such an approach to the hydrogen economy will however produce considerable carbon dioxide. Hence, any technology for hydrocarbon or coal reforming to hydrogen must be compatible for conveniently facilitating carbon dioxide sequestration.

Membrane technologies can achieve this goal in a spontaneous overall process. This is illustrated by considering the following process steps shown schematically in Figure 4. Step 1 involves initial reforming of the carbonaceous feedstock using oxygen transport membrane technology into a mixture of carbon monoxide and hydrogen. This mixture is subsequently subjected to the water-gas shift reaction (Step 2) whereby residual carbon monoxide in the presence of introduced steam is converted to carbon dioxide and hydrogen. Application of hydrogen separation membrane technology in Step 3 permits one

to both sequester the carbon dioxide and supply hydrogen to either a fuel cell (Step 4) or to a conventional combustion unit (Step 5). The overall process leading to a hydrogen feedstock from a carbonaceous feed is thermodynamically downhill.

How hydrogen combustion would be incorporated into an environmentally benign electric utility plant whereby separated carbon dioxide could be used to either cogenerate hydrocarbon feedstock or be sequestered is illustrated in Figure 5.

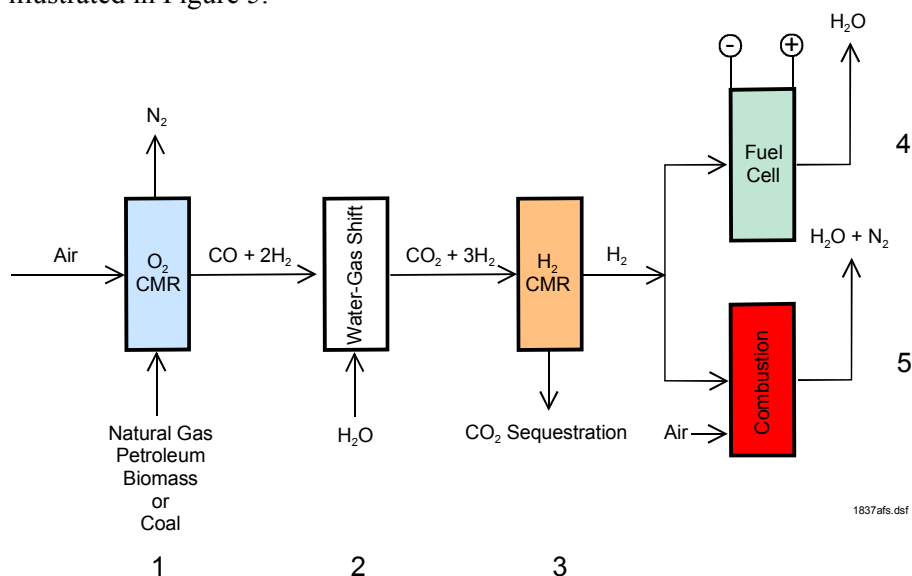


Figure 4. Integration of oxygen and hydrogen transport membranes for supply of a pure hydrogen feedstream.

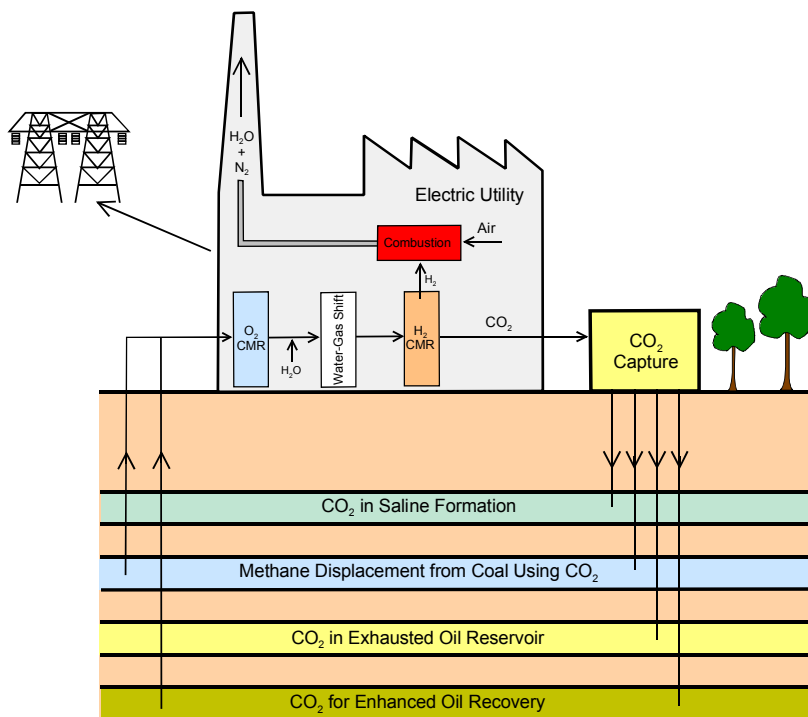


Figure 5. Strategy for disposing of membrane separated CO_2 from an electric utility.

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